(12) **EUROPEAN PATENT SPECIFICATION**

(54) **METHOD AND APPARATUS FOR OBTAINING ENHANCED PRODUCTION RATE OF THERMAL CHEMICAL REACTIONS**

VERFAHREN UND VORRICHTUNG ZUR GEWINNUNG ERHÖHTER PRODUKTIONSRATEN IN THERMOCHEMISCHEN REAKTIONEN

PROCEDE ET DISPOSITIF PERMETTANT D'AMELIORER LE COEFFICIENT DE PRODUCTION DES REACTIONS CHIMIQUES THERMIQUES

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Description

FIELD OF THE INVENTION

[0001]   The present invention relates to a method and apparatus for thermal chemical reactions. More specifically, the method and apparatus provide an enhanced reaction rate for the thermal chemical reaction.

[0002]   As used herein, the term thermal chemical reaction(s) includes exothermic and endothermic chemical reactions.

BACKGROUND OF THE INVENTION

[0003]   Thermal chemical reactions including exothermic and endothermic chemical reactions are well known. Examples of thermal chemical reactions include but are not limited to Hydrogen and Hydrocarbon conversion reactions including but not limited to steam reforming, water-gas shift reactions and combustion are well known. These reactions are usually carried out in the presence of a catalyst at temperatures up to about 1000 °C . Because the intrinsic kinetics of the thermal chemical reaction are much faster than the heat transfer rate between the reaction vessel and the thermal sink or environment, the rate of product production is limited. Limited production rates may be characterized in terms of residence time which is typically seconds to minutes in convention thermal chemical reaction vessels.

[0004]   For example, the water gas shift reaction is conventionally carried out in fixed bed reactors. The water gas shift reaction of converting carbon monoxide and water to carbon dioxide and hydrogen suffers from multiple-second residence times (kinetic impediment) when carried out in fixed bed reactors. Theoretical kinetics suggests possible residence times on the order of milliseconds. There are two kinetic retarding aspects to conventional reactors. The first is a diffusion limitation as reactants diffuse into and out of a catalyst bearing porous pellet and the second is a heat transfer limitation which is a combination of heat transfer parameters (conduction, length) of catalyst supports and overall reactor geometry (shape and size). Because the water gas shift reaction is critical to a multi-reactor fuel processing system that supports distributed energy production through the use of a fuel cell, there is a need for a smaller, faster water gas shift reactor.

[0005]   Another example is conventional methane steam reforming reactor produces synthesis gas at an average residence time of several seconds and with an effectiveness factor of 0.01 to 0.05 reported by Adris, A., Pruden, B., Lim, C., J. Grace, 1996, On the reported attempts to radically improve the performance of the steam methane reforming reactor, Canadian Journal of Chemical Engineering, 74, 177-186. In typical industrial operation, the methane to steam ratio is run at 3:1 to prevent coke formation.

[0006]   Efforts to improve heat transfer between the reaction vessel and the thermal sink have made only modest improvements in product production rate. Thus, there is a need in the art of thermal chemical reactions for a method and apparatus that increases the heat transfer rate between the reaction vessel and the thermal sink and thereby approach the theoretical intrisic kinetic rate of reaction and production.

[0007]   In US-A-4795618 heat transfer was promoted by the use of a reaction section and a heat transfer section, both of which are connected by a gas-tight highly heat conductive boundary layer, where both the reaction section and the heat transfer section comprise a porous heat conductive material such as porous sintered metal.

[0008]   In WO-A-9632188 similar principles are used, but a second reaction section is used rather than a heat transfer section so that an exothermic reaction in one reaction section can transfer heat to the other reaction section where an endothermic reaction takes place.

SUMMARY OF THE INVENTION

[0009]   According to one aspect of the present invention there is provided a method for obtaining a product at an enhanced production rate for a thermal chemical reaction per reaction chamber volume of a reaction chamber (102 or 104) having an inlet and an outlet for a thermal chemical reaction, the method comprising the steps of:

(a) passing a reactant flow through a porous insert within said reaction chamber (102 or 104), wherein the reactant flow substantially completely passes through said porous insert, wherein said reaction chamber volume with said porous insert has a mean porosity of less than 1 and a mass transport distance no greater than 3mm;
(b) transferring reaction heat through said porous insert, said reaction chamber (102 or 104) having a length parallel to a bulk reactant flow, said length less than or equal to 15cm (6 inches), and with a height less than or equal to 5cm (2 inches); and
(c) transferring heat through a heat transfer chamber in thermal contact with the reaction chamber volume, said heat transfer chamber comprising an inlet and an outlet and an open space for flow of a heat exchange fluid, and said heat being transferred through a wall between the heat transfer chamber and the reaction chamber (102 or 104).

[0010]   According to another aspect of the present invention there is provided a reactor for obtaining an enhanced

production rate per reaction chamber volume of a reaction chamber (102 or 104) for a thermal chemical reaction, the reactor comprising:

(a) a porous insert within said reaction chamber (102 or 104), wherein, during operation, reactant flow substantially completely passes through said porous insert, wherein said reaction chamber (102 or 104) with said porous insert has a mean porosity of less than 1 and a mass transport distance no greater than 3 mm; and

(b) said reaction chamber volume having an inlet and an outlet, a length parallel to a bulk reactant flow, said length being less than or equal to 15 cm (6 inches), and a height less than or equal to 5 cm (2 inches).

[0011] These features have been found to cooperate with the reaction kinetics in terms of transferring heat at a rate sufficient to avoid substantial impediment of the kinetics. These features are effective for both catalytic and non-catalytic thermal chemical reactions. For catalytic chemical reactions, addition of a catalyst upon the porous insert permits flow of reactants past catalyst sites rather than limiting reactant motion to diffusion as in conventional systems. Thus, according to the present invention, for catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics. More specifically a water gas shift reactor made according to the present invention has 1/10th to 1/100th the size of conventional processing hardware for the same production output.

[0012] Both the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1a is a cross section of a stacked reaction chamber with heat exchanger chamber.

FIG. 1b is an isometric of a nested reaction chamber with heat exchanger chamber.

FIG. 2a is a graph of percent selectivity versus residence time for long contact time water gas shift with a powder catalytic porous insert.

FIG. 2b is a graph of percent selectivity versus residence time for short contact time water gas shift with a powder catalytic porous insert.

FIG. 3 is a graph of percent selectivity versus temperature for various residence times for water gas shift with a coated metal foam porous insert.

FIG. 4 is a graph of methane conversion versus temperature for various residence times for a steam to methane ratio of 2.5:1.

FIG. 5a is a graph of conversion and selectivity versus time for n-butane steam reforming with a porous insert of a porous substrate with interfacial layer and catalyst material.

FIG. 5b is a graph of conversion and selectivity versus time for n-butane steam reforming with a regenerated porous insert.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0014] Referring to **FIG.'s 1a** and **1b**, a vessel **100** for thermal chemical reactions the vessel having two chambers **102** and **104** with a wall **106** therebetween. Either of the two chambers **102, 104** may be the reaction chamber. Bulk flow of reactants within the reaction chamber **102** is substantially perpendicular to a cross section plane **108**. The vessel **100** may have stacked chambers as in FIG. 1 a or nested chambers as in FIG. 1b. The reaction in the reaction chamber may be endothermic or exothermic.

[0015] In a thermal chemical reaction, the rate of production (reaction kinetics) is limited by the rate of heat transfer either to (endothermic) or from (exothermic) the reaction site. In order to obtain an enhanced heat transfer rate and thereby an enhanced production rate, the reaction chamber has a porous insert (not shown) within the reaction chamber volume wherein the reaction chamber volume with the porous insert has a mean porosity less than 1 and a transport distance no greater than 3 mm, thereby transferring reaction heat at an enhanced heat transfer rate through the porous insert.

[0016] The porous insert may be a powder, a porous monolith (including but not limited to metal or ceramic foam, honeycomb, tube bank, stacked microchannel assembly, and combinations thereof), fibers (e.g. steel wool), or combinations thereof. In view of the cost of replacing spent catalyst, for catalytic reactors, it is preferred that the porous insert be removable from the reaction chamber. The porous insert may be arranged to provide single or multiple flow passages for reactants through the reaction chamber volume. The porous insert may rest on or contact raised features formed on

the interior surface(s) of the reaction chamber.

[0017] For catalytic thermal chemical reactions, a preferred porous insert is a porous support with a catalyst material thereon. More preferred is a porous insert with a solution deposited interfacial layer between the porous support and the catalyst material. A more preferred porous insert has a buffer layer between the porous support and the interfacial layer.

[0018] In addition, the reaction chamber volume has a length parallel to a bulk reactant flow, the length less than or equal to 15.24 cm (6 inches) and has a height less than or equal to 5.08 cm (2 inches). The limited length and height provide short distances for the projections thereby permitting faster heat transfer. Moreover, the short length reduces overall pressure drop through the reaction chamber.

[0019] The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall 106 between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction.

[0020] The interfacial layer is a solution deposited metal oxide. The solution deposited metal oxide includes but is not limited to γAl_2O_3, SiO_2, ZrO_2, TiO_2, magnesium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof. Typically the porous support has a thermal coefficient of expansion different from that of the interfacial layer. Accordingly, for high temperature catalysis (T > 150 °C) a buffer layer is needed to transition between the two coefficients of thermal expansion.

[0021] The buffer layer is a metal oxide that is Al_2O_3, TiO_2 and combinations thereof. More specifically, the Al_2O_3 is α-Al_2O_3, γ-Al_2O_3 and combinations thereof. The structure of the α-Al_2O_3 is preferred because TiO_2 is not as a good material as alumina against oxygen diffusion. Therefore, it is expected that resistance against high temperature oxidation can be improved with alumina coated foam. When the porous substrate 100 is metal foam, a preferred embodiment has a buffer layer formed of two sub-layers. The first sublayer is α-Al_2O_3 for passivating the metal foam and the second layer is TiO_2 for bonding to the interfacial layer.

[0022] Deposition of the buffer layer 102 may be by vapor deposition including but not limited to chemical vapor deposition, physical vapor deposition or combinations thereof. Because the vapor deposition is conducted at high temperatures, polycrystalline phases are formed providing good adhesion of the metal oxide to the metal foam surface.

[0023] Alternatively, the buffer layer 102 may be obtained by solution coating. The solution coating has the steps of metal surface functionalization via hydroxide formation, followed by surface hydrolysis of alkoxides to obtain the polycrystalline phases. This solution coating may be preferred as a lower cost method of depositing the buffer layer 102.

[0024] Polycrystalline metal oxides resist flaking off under thermal cyclings. The open cells of a metal foam may range from about 7.9 pores/cm (20 ppi) to about 393.7 pores/cm (1000 ppi) and is preferably about 31.5 pores/cm (80 ppi). The catalyst material (when used) is deposited onto the interfacial layer. The catalyst material may be any catalyst metal including but not limited to noble metal, transition metal and combinations thereof, or a catalyst metal oxide or transition metal oxide including but not limited to magnesium oxide, titanium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, zirconium oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, silicon oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof.

[0025] The method of making the preferred catalyst has the steps of selecting a porous support, vapor depositing a buffer layer on the porous support, solution depositing a interfacial layer thereon, and depositing a catalyst metal onto the interfacial layer. When a metal foam is used as the porous support, the metal foam is etched prior to vapor depositing the buffer layer. Etching is preferably with an acid, for example HCl. Optionally a catalyst layer may be deposited onto the interfacial layer.

Example 1

[0026] An experiment was conducted to demonstrate a chemical thermal reactor according to the present invention using the water gas shift reaction.

[0027] A first porous insert was made with a catalyst material of a pre-reduced and stabilized 5-wt% Ru/ZrO$_2$ catalyst (1/8-inch extrudates) obtained from Degussa Corporation. The catalyst material was ground and sieved to 65 to 100 mesh.

[0028] A second porous insert was made with Ni metal foam with 31.5 pores/cm (80 pores per inch) (ppi) machined to fit in a 7 mm ID quartz tube, ranging from 0.5 to 2.5 cm in length. The metal foam was washed in a sonicator with acetone, chloroform, and water successively over 10-minute intervals. It was also etched in a 1 M HCl solution at 60 °C for 30 min. The etched metal foam was saturated with a zirconium n-propoxide/1-propanol solution (Aldrich), followed by ambient hydrolysis with water vapor for 72 h, then calcined at 450 °C for 4 h to form the interfacial layer. The ZrO_2-coated metal foam was saturated with a dilute aqueous RuCl$_3$ solution (RuCl$_3$ hydrate, Aldrich). The saturation process was repeated several times until the desired Ru loading was achieved. The coated metal foam supported Ru catalyst was finally dried at 100 °C in vacuum overnight, followed by calcination at 350 °C for 1 h. Prior to testing, the catalyst was activated with a 10%H$_2$/He mixture at 350 °C for at least 1 h.

[0029] A catalytic plug flow reactor (PFR) system was used to test both porous inserts. The PFR was configured in a single-zone furnace as the heat transfer chamber. The reactor system included a steam generator placed directly prior to the reactor inlet, a PFR housed within the furnace, and a condenser located at the reactor outlet. The porous insert was packed in a 7 mm ID quartz tube, which was necked at the center.

[0030] The feed water was fed to the steam generator using a Cole Parmer syringe pump. Carbon monoxide and nitrogen (a diluent) were fed to the system using Matheson mass flow controllers. The mixed feed stream flowed through the steam generator before entering the PFR in a downflow fashion. The product gases were directed through the condenser and sent to an on-line gas chromatograph, where the product stream was analyzed.

[0031] Two thermocouples were placed inside the catalytic PFR system. One thermocouple was located above the porous insert. The second thermocouple was placed adjacent to the porous insert outside of the quartz tube to measure the furnace temperature. A pressure gauge at the reactor inlet was used to measure the differential pressure across the porous insert.

[0032] The product gases were analysed immediately upon exit from the reactor with a Microsensor Technology Inc., (MTI) M200 Gas Chromatograph. Using a 10-m molecular sieve column (argon carrier gas, 100°C, 234.9 kPa (34.1 psig)) and an 8-m PoraplotU column (helium carrier gas, 65°C 185.3 kPa (26.9 psig)) in parallel, the GC analyzes for hydrogen, nitrogen, oxygen, methane, carbon monoxide, air, carbon dioxide, ethane, and ethylene in 75 sec. The M200 used a vacuum pump to draw a small sample from the product stream with a 40-sec purge and a 100-millisecond injection time. Water was removed from the gas stream prior to entering the M200.

[0033] Carbon monoxide conversion was calculated based on the moles of material in the inlet and outlet gas stream, as shown in equation 1. The selectivity to carbon dioxide (and hydrogen) or methane was calculated in equations 2 and 3, respectively.

$$X_{CO} = 100 * (n_{CO\text{-}in} - n_{CO\text{-}out})/ n_{CO\text{-}in} \qquad (1)$$

$$S_{CO2} = 100 * n_{CO2}/ (n_{CO2} + n_{CH4}) \qquad (2)$$

$$S_{CH4} = 100 - S_{CO2} \qquad (3)$$

[0034] Using the first porous insert, fine catalyst powders (65 to 100 mesh), the intrinsic reaction kinetics were approximately measured. The contact time varied from 10 milliseconds to 1 sec. **FIG.'s 2a** and **2b** show the performance for long and short contact times. At 300 °C and a steam to carbon ratio of 3:1, 25 milliseconds on the Ru-based catalyst was sufficient to convert greater than 98% of the carbon monoxide to carbon dioxide and hydrogen. At 50 milliseconds, a CO conversion of 99.8 % was measured with a selectivity of 100% to the desired products (CO_2 and H_2). The equilibrium conversion of CO at 300 °C and a steam to carbon ratio of 3:1 was 99.93%.

[0035] Tests run with longer contact times (> 100 milliseconds) showed the formation of methane, which has an equilibrium selectivity of 22.82%. The equilibrium selectivity line for carbon dioxide and hydrogen is shown on FIG. 2a. As the contact time increased, the formation of methane also increased. A software package, FACT™, was used for all equilibrium calculations.

[0036] The results with the second porous insert (coated metal foam) are shown in **FIG. 3.** At 300 °C, the CO conversion was less than 10%. However, at 500 °C and a steam to carbon ratio of 3:1, the measured carbon monoxide conversion reached 94% with a contact time of 50 milliseconds. The equilibrium conversion was 94.53% at these conditions. With a contact time as short as 10 milliseconds, the carbon monoxide conversion exceeded 90% and 100% selectivity to carbon dioxide and hydrogen was observed. The equilibrium CO_2 selectivity was 93.52% at 500 °C.

[0037] At the contact times of 10, 50, and 100 milliseconds, the measured selectivity remained near 100%, with methane below the detectability limit of the GC. These findings showed that desired non-equilibrium chemistry was exploited in the coated metal foam. Unwanted series and slow parallel reaction pathways, such as the formation of methane, were effectively shut down.

[0038] The second porous insert of the coated metal foam had a higher activation temperature than the first porous insert of catalyst powder for two reasons. First, the catalyst washcoat had a slightly different composition and structure than the catalyst powders. Independent catalyst tests with powders made from the same washcoat verified the higher required activation temperature. The other distinction between the two porous inserts was a reduced weight of active catalyst (approximately 10%) on the coated metal foam.

Example 2

[0039]   An experiment was conducted to demonstrate hydrocarbon steam reforming according to the present invention.

[0040]   Using the first porous insert (powder) as in Example 1, methane steam reforming was achieved with 100% conversion at 850°C in 25 milliseconds on a 5%Rh/γ-Al$_2$O$_3$ catalyst (**FIG. 4**). Using the second porous insert (coated metal foam) as in Example 1, with a 5%Rh/γ-Al$_2$O$_3$ catalyst/interfacial layers on 31.5 pores.cm (80 ppi) stainless steel metal foam reduced the operating temperature by 100°C to achieve the same performance at 750°C.

[0041]   No coke formation was observed during any of the millisecond residence time experiments with lower steam to methane ratios (2.5:1).

[0042]   Results for other hydrocarbons are shown in Table E2-1 wherein "time" is residence time.

Table E2-1: Preliminary hydrocarbon reforming data based on 5%Rh/γ-Al$_2$O$_3$ catalyst screening tests

Hydrocarbon	Temperature (C)	Time (ms)	Conversion %	H2 Sel. %
Butane	600	25	100	96
Gasoline	800	50	95	~ 95
Iso-octane[A]	700	25	100	89.5
Kerosene	600	50	95	~ 98
[A] Catalyst material included a titania buffer layer				

[0043]   Further data for an n-butane steam reforming experiment are shown in **FIG. 5a**. A porous insert of 31.5 pores/cm (80 ppi) stainless steel with an interfacial layer of alumina and a catalyst material of rhodium (15.6 wt% Rh on 17.1 wt% alumina, balance stainless steel foam, no buffer layer). Conditions were 650°C at 95 ms residence time with a steam to carbon ratio of 3.58:1. The pressure drop increased from negligible to over 48.2 kPa (7 psig) attributed to cracking and spalling of the interfacial and catalyst layers. The catalyst was regenerated in air to remove deposited carbon. **FIG. 5b** shows poorer performance. Pressure drop increased to over 48.2 kPa (7 psig) after only 5 operating hours in two days.

Claims

1.   A method for obtaining a product at an enhanced production rate for a thermal chemical reaction per reaction chamber volume of a reaction chamber (102 or 104) having an inlet and an outlet for a thermal chemical reaction, the method comprising the steps of:

(a) passing a reactant flow through a porous insert within said reaction chamber (102 or 104), wherein the reactant flow substantially completely passes through said porous insert, wherein said reaction chamber volume with said porous insert has a mean porosity of less than 1 and a mass transport distance no greater than 3mm;

(b) transferring reaction heat through said porous insert, said reaction chamber (102 or 104) having a length parallel to a bulk reactant flow, said length less than or equal to 15cm (6 inches), and with a height less than or equal to 5cm (2 inches); and

(c) transferring heat through a heat transfer chamber in thermal contact with the reaction chamber volume, said heat transfer chamber comprising an inlet and an outlet and an open space for flow of a heat exchange fluid, and said heat being transferred through a wall between the heat transfer chamber and the reaction chamber (102 or 104).

2.   The method as recited in claim 1, wherein a catalyst is on the porous insert.

3.   The method as recited in claim 2, wherein said porous insert has an interfacial layer thereon, and a catalyst metal on the interfacial layer.

4.   The method as recited in claim 3, wherein said porous insert has a buffer layer between the porous support and the interfacial layer.

5.   The method as recited in claim 4, wherein said buffer layer is a metal oxide.

6. The method as recited in claim 5, wherein said metal oxide is selected from the group consisting of Al_2O_3, TiO_2 and combinations thereof.

7. The method as recited in claim 6, wherein said Al_2O_3 is selected from the group consisting of α -Al_2O_3, γ -Al_2O_3, other phases of Al_2O_3, and combinations thereof.

8. The method as recited in any of claims 4 to 7 wherein said buffer layer is vapour-deposited.

9. The method as recited in any of claims 4 to 8 wherein said buffer layer comprises a plurality of sublayers.

10. The method as recited in any if claim 3 to 9, wherein the interfacial layer is solution-deposited.

11. The method as recited in claim 10, wherein said solutions deposited metal oxide is selected from the group consisting of γ - Al_2O_3, SiO_2, ZrO_2, TiO_2 and combinations thereof.

12. The method as recited in any of claims 3 to 11 wherein the interfacial layer comprises a metal oxide.

13. The method as recited in any of claims 2 to 12, wherein said catalyst material is a metal selected from the group of noble metal, transition metal and combinations thereof.

14. The method as recited in any of the preceding claims, wherein said porous insert comprises a porous ceramic.

15. The method as recited in any of the preceding claims wherein the porous insert comprises a porous monolith.

16. The method as recited in any of the claims 1-13 wherein the porous insert comprises a metal foam.

17. The method as recited in any of the preceding claims wherein the porous insert is in thermal contact with walls of the reaction chamber (102 or 104) and has 8 pores per cm (20 pores per inch) to 400 pores per cm (1000 pores per inch).

18. The method as recited in any of the preceding claims, wherein said thermal chemical reaction is a catalytic chemical reaction.

19. The method as recited in any of the preceding claims, wherein said thermal chemical reaction is a steam reforming thermal chemical reaction and said reactant flow comprises a hydrocarbon.

20. The method as recited in claim 19, wherein said porous insert comprises a porous support with a catalyst material thereon, such that 80% to 100% equilibrium conversion of said hydrocarbon is converted at a residence time of less than about 50 milliseconds.

21. The method of claim 20 wherein the residence time is 11 to 50 milliseconds.

22. The method of claim 21 wherein the porous insert comprises a metal foam support, an interfacial layer; and wherein the reaction takes place at 600 to 950°C.

23. The method of claim 22 wherein the hydrocarbon is selected from the group consisting of butane, gasoline, iso-octant, and kerosene; and wherein hydrogen is produced with a selectivity of 89% to 98%.

24. The method as recited in any of claims 1 to 18, wherein said thermal chemical reaction is a water gas shift thermal chemical reaction, and said reactant flow comprises water and carbon monoxide.

25. The method as recited in claim 24, wherein said porous insert comprises a porous support with a catalyst material thereon, and said contact time is less than about 100 milliseconds, such that conversion of carbon monoxide is greater than about 50% of equilibrium conversion.

26. The method if claim 25 wherein the contact time is between 10 and 100 milliseconds, the conversion is greater than 80%, and the method has a selectivity of at least about 100% of equilibrium selectivity to carbon dioxide.

27. The method of claim 26 where the porous insert comprises a metal formed supported Ru catalyst.

28. A reactor for obtaining an enhanced production rate per reaction chamber volume of a reaction chamber (102 or 104) for a thermal chemical reaction, the reactor comprising:

(a) a porous insert within said reaction chamber (102 or 104), wherein, during operation, reactant flow substantially completely passes through said porous insert, wherein said reaction chamber (102 or 104) with said porous insert has a mean porosity of less than 1 and a mass transport distance no greater than 3 mm; and
(b) said reaction chamber volume having an inlet and an outlet, a length parallel to a bulk reactant flow, said length being less than or equal to 15 cm (6 inches), and a height less than or equal to 5 cm (2 inches).

29. The reactor as recited in claim 28, wherein a catalyst material is on the porous insert.

30. The reactor as recited in claim 29, wherein said porous insert has a solution-deposited interfacial layer between a porous support and the catalyst material.

31. The reactor as recited in claim 30, wherein said porous insert has a buffer layer between the porous support and the solution deposited interfacial layer.

32. The reactor as recited in claim 31, wherein said buffer layer is a metal oxide.

33. The reactor as recited in claim 32, wherein said metal oxide is selected from the group consisting of Al_2O_3, TiO_2 and combination thereof.

34. The reactor as recited in claim 33, wherein said Al_2O_3 is selected from the group consisting of α -Al_2O_3, γ -Al_2O_3, other phases of Al_2O_3, and combinations thereof.

35. The reactor as recited in any of claims 31 to 34 wherein said buffer layer us vapour deposited.

36. The reactor as recited in any of claims 31 to 35 wherein said buffer layer comprises a plurality of sublayers.

37. The reactor as recited in any of claims 30 to 36, wherein the interfacial layer is solution-deposited.

38. The reactor as recited in claim 37, wherein said solution-deposited metal oxide is selected from the group consisting of γ -Al_2O_3, SiO_2, ZrO_2, TiO_2 and combinations thereof.

39. The reactor of any of claims 30 to 38 wherein the solution-deposited interfacial layer comprises a metal oxide.

40. The reactor as recited in any of claims 29 to 39, wherein said catalyst material is a metal selected from the group of noble metal, transition metal and combinations thereof.

41. The reactor as recited in any of claims 28 to 40, wherein the porous insert comprises a porous ceramic.

42. The reactor as recited in any of claims 28 to 41 wherein the porous insert comprises a porous monolith.

43. The reactor as recited in any of claims 28 to 40 wherein the porous insert comprises a metal foam.

44. The reactor as recited in any of claims 28 to 43 wherein the porous insert comprises a metal or ceramic foam and is in thermal contact with walls of the reaction chamber (102 or 104) and has 8 pores per cm (20 pores per inch) to 400 pores per cm (1000 pores per inch).

45. A vessel (100) for obtaining an enhanced production rate per reaction chamber volume of a reaction chamber (102 or 104) for a thermal chemical reaction, the vessel (100) comprising:

(a) a reactor as recited in any of claims 28-44; and
(b) a heat transfer chamber in thermal contact with the reaction chamber volume, said heat transfer chamber having an inlet and outlet, an open space for a flow of a heat exchange fluid, and a wall disposed between the heat transfer chamber and the reaction chamber (102 or 104), such that, during operation, heat transfers across

said wall.

Patentansprüche

1. Verfahren zum Erhalten eines Produktes bei einer erhöhten Produktionsgeschwindigkeit für eine thermische chemische Reaktion pro Reaktionskammervolumen einer Reaktionskammer (102 oder 104) mit einem Einlaß und einem Auslaß für eine thermische chemische Reaktion, wobei das Verfahren die Schritte umfaßt:

   (a) das Leiten eines Reaktandenflusses durch einen porösen Einsatz innerhalb der Reaktionskammer (102 oder 104), wobei der Reaktandenfluß im wesentlichen vollständig durch den porösen Einsatz geleitet wird, wobei das Reaktionskammervolumen mit dem porösen Einsatz eine mittlere Porosität von weniger als 1 und eine Massentransportentfernung von nicht größer als 3 mm aufweist,
   (b) das Übertragen der Reaktionswärme durch den porösen Einsatz, wobei die Reaktionskammer (102 oder 104) eine Länge parallel zu einem Hauptreaktandenfluß aufweist, wobei die Länge weniger als oder gleich 15 cm (6 Inch) ist, und eine Höhe weniger als oder gleich 5 cm (2 Inch) aufweist, und
   (c) das Übertragen von Wärme durch eine Wärmeübertragungskammer in thermischem Kontakt mit dem Reaktionskammervolumen, wobei die Wärmeübertragungskammer einen Einlaß und einen Auslaß und einen offenen Raum zum Fluß einer Wärmeaustauschflüssigkeit umfaßt, und wobei die Wärme durch eine Wand zwischen der Wärmeübertragungskammer und der Reaktionskammer (102 oder 104) übertragen wird.

2. Verfahren nach Anspruch 1, wobei sich ein Katalysator auf dem porösen Einsatz befindet.

3. Verfahren nach Anspruch 2, wobei der poröse Einsatz eine Zwischenschicht darauf und ein Katalysatormetall auf der Zwischenschicht aufweist.

4. Verfahren nach Anspruch 3, wobei der poröse Einsatz eine Pufferschicht zwischen dem porösen Träger und der Zwischenschicht aufweist.

5. Verfahren nach Anspruch 4, wobei die Pufferschicht ein Metalloxid ist.

6. Verfahren nach Anspruch 5, wobei das Metalloxid aus der Gruppe, bestehend aus Al_2O_3, TiO_2 und Kombinationen davon, ausgewählt ist.

7. Verfahren nach Anspruch 6, wobei das Al_2O_3 aus der Gruppe, bestehend aus α-Al_2O_3, γ-Al_2O_3, anderen Phasen von Al_2O_3 und Kombinationen davon, ausgewählt ist.

8. Verfahren nach einem der Ansprüche 4 bis 7, wobei die Pufferschicht dampfabgeschieden ist.

9. Verfahren nach einem der Ansprüche 4 bis 8, wobei die Pufferschicht eine Vielzahl an Unterschichten umfaßt.

10. Verfahren nach einem der Ansprüche 3 bis 9, wobei die Zwischenschicht lösungsabgeschieden ist.

11. Verfahren nach Anspruch 10, wobei das lösungsabgeschiedene Metalloxid aus der Gruppe, bestehend aus γ-Al_2O_3, SiO_2, ZrO_2, TiO_2 und Kombinationen davon, ausgewählt ist.

12. Verfahren nach einem der Ansprüche 3 bis 11, wobei die Zwischenschicht ein Metalloxid umfaßt.

13. Verfahren nach einem der Ansprüche 2 bis 12, wobei das Katalysatormaterial ein Metall, ausgewählt aus der Gruppe von Edelmetallen, Übergangsmetallen und Kombinationen davon, ist.

14. Verfahren nach einem der vorstehenden Ansprüche, wobei der poröse Einsatz eine poröse Keramik umfaßt.

15. Verfahren nach einem der vorstehenden Ansprüche, wobei der poröse Einsatz einen porösen Monolithen umfaßt.

16. Verfahren nach einem der Ansprüche 1 bis 13, wobei der poröse Einsatz einen Metallschaum umfaßt.

17. Verfahren nach einem der vorstehenden Ansprüche, wobei sich der poröse Einsatz in thermischem Kontakt mit

Wänden der Reaktionskammer (102 oder 104) befindet und 8 Poren pro cm (20 Poren pro Inch) bis 400 Poren pro cm (1000 Poren pro Inch) aufweist.

18. Verfahren nach einem der vorstehenden Ansprüche, wobei die thermische chemische Reaktion eine katalytische chemische Reaktion ist.

19. Verfahren nach einem der vorstehenden Ansprüche, wobei die thermische chemische Reaktion eine thermische chemische Dampfreforming-Reaktion ist und der Reaktandenfluß einen Kohlenwasserstoff umfaßt.

20. Verfahren nach Anspruch 19, wobei der poröse Einsatz einen porösen Träger mit einem Katalysatormaterial darauf umfaßt, so daß 80% bis 100% Gleichgewichtsumwandlung des Kohlenwasserstoffs bei einer Verweildauer von weniger als etwa 50 Millisekunden umgewandelt wird.

21. Verfahren nach Anspruch 20, wobei die Verweildauer 11 bis 50 Millisekunden beträgt.

22. Verfahren nach Anspruch 21, wobei der poröse Einsatz einen Metallschaumträger und eine Zwischenschicht umfaßt, und wobei die Reaktion bei 600 bis 950°C stattfindet.

23. Verfahren nach Anspruch 22, wobei der Kohlenwasserstoff aus der Gruppe, bestehend aus Butan, Benzin, Isooctan und Kerosin, ausgewählt ist, und wobei Wasserstoff mit einer Selektivität von 89 bis 98% hergestellt wird.

24. Verfahren nach einem der Ansprüche 1 bis 18, wobei die thermische chemische Reaktion eine thermische chemische Wassergasreaktion ist, und wobei der Reaktandenfluß Wasser und Kohlenmonoxid umfaßt.

25. Verfahren nach Anspruch 24, wobei der poröse Einsatz einen porösen Träger mit einem Katalysatormaterial darauf umfaßt, und die Kontaktdauer weniger als etwa 100 Millisekunden beträgt, so daß die Umwandlung von Kohlenmonoxid größer als etwa 50% der Gleichgewichtsumwandlung ist.

26. Verfahren nach Anspruch 25, wobei die Kontaktdauer zwischen 10 und 100 Millisekunden beträgt, die Umwandlung größer als 80% ist, und das Verfahren eine Selektivität von mindestens etwa 100% der Gleichgewichtsselektivität zu Kohlendioxid aufweist.

27. Verfahren nach Anspruch 26, wobei der poröse Einsatz einen Metallschaumgetragenen Ru-Katalysator umfaßt.

28. Reaktor zum Erhalten einer erhöhten Produktionsgeschwindigkeit pro Reaktionskammervolumen einer Reaktionskammer (102 oder 104) für eine thermische chemische Reaktion, wobei der Reaktor umfaßt:

(a) einen porösen Einsatz innerhalb der Reaktionskammer (102 oder 104), wobei während des Betriebs der Reaktandenfluß im wesentlichen vollständig durch den porösen Einsatz geleitet wird, wobei die Reaktionskammer (102 oder 104) mit dem porösen Einsatz eine mittlere Porosität von weniger als 1 und eine Massentransportentfernung von nicht größer als 3 mm aufweist, und
(b) wobei das Reaktionskammervolumen einen Einlaß und einen Auslaß, eine Länge parallel zu einem Hauptreaktandenfluß, wobei die Menge weniger als oder gleich 15 cm (6 Inch) ist, und eine Höhe von weniger als oder gleich 5 cm (2 Inch) aufweist.

29. Reaktor nach Anspruch 28, wobei ein Katalysatormaterial auf dem porösen Einsatz angeordnet ist.

30. Reaktor nach Anspruch 29, wobei der poröse Einsatz eine lösungsabgeschiedene Zwischenschicht zwischen einem porösen Träger und dem Katalysatormaterial aufweist.

31. Reaktor nach Anspruch 30, wobei der poröse Einsatz eine Pufferschicht zwischen dem porösen Träger und der lösungsabgeschiedenen Zwischenschicht aufweist.

32. Reaktor nach Anspruch 31, wobei die Pufferschicht ein Metalloxid ist.

33. Reaktor nach Anspruch 32, wobei das Metalloxid aus der Gruppe, bestehend aus Al_2O_3, TiO_2 und Kombinationen davon, ausgewählt ist.

34. Reaktor nach Anspruch 33, wobei das Al_2O_3 aus der Gruppe, bestehend aus α-Al_2O_3, γ-Al_2O_3, anderen Phasen von Al_2O_3 und Kombinationen davon, ausgewählt ist.

35. Reaktor nach einem der Ansprüche 31 bis 34, wobei die Pufferschicht dampfabgeschieden ist.

36. Reaktor nach einem der Ansprüche 31 bis 35, wobei die Pufferschicht eine Vielzahl an Unterschichten umfaßt.

37. Reaktor nach einem der Ansprüche 30 bis 36, wobei die Zwischenschicht lösungsabgeschieden ist.

38. Reaktor nach Anspruch 37, wobei das lösungsabgeschiedene Metalloxid aus der Gruppe, bestehend aus γ-Al_2O_3, SiO_2, ZrO_2, TiO_2 und Kombinationen davon, ausgewählt ist.

39. Reaktor nach einem der Ansprüche 30 bis 38, wobei die lösungsabgeschiedene Zwischenschicht ein Metalloxid umfaßt.

40. Reaktor nach einem der Ansprüche 29 bis 39, wobei das Katalysatormaterial ein Metall, ausgewählt aus der Gruppe von Edelmetall, Übergangsmetall und Kombinationen davon, ist.

41. Reaktor nach einem der Ansprüche 28 bis 40, wobei der poröse Einsatz eine poröse Keramik umfaßt.

42. Reaktor nach einem der Ansprüche 28 bis 41, wobei der poröse Einsatz einen porösen Monolithen umfaßt.

43. Reaktor nach einem der Ansprüche 28 bis 40, wobei der poröse Einsatz einen Metallschaum umfaßt.

44. Reaktor nach einem der Ansprüche 28 bis 43, wobei der poröse Einsatz ein Metall oder keramischen Schaum umfaßt und sich in thermischem Kontakt mit Wänden der Reaktionskammer (102 oder 104) befindet und 8 Poren pro cm (20 Poren pro Inch) bis 400 Poren pro cm (1000 pro Inch) aufweist.

45. Gefäß (100) zum Erhalten einer erhöhten Produktionsgeschwindigkeit pro Reaktionskammervolumen einer Reaktionskammer (102 oder 104) für eine thermische chemische Reaktion, wobei das Gefäß (100) umfaßt:

(a) einen Reaktor nach einem der Ansprüche 28 bis 44 und
(b) eine Wärmeübertragungskammer in thermischem Kontakt mit dem Reaktionskammervolumen, wobei die Wärmeübertragungskammer einen Einlaß und Auslaß, einen offenen Raum für einen Fluß einer Wärmeaustauschflüssigkeit und eine zwischen der Wärmeübertragungskammer und der Reaktionskammer (102 oder 104) angeordnete Wand aufweist, so daß während des Betriebs Wärme durch die Wand übertragen wird.

Revendications

1. Procédé pour obtenir un produit à une vitesse de production améliorée pour une réaction chimique thermique par volume de chambre réactionnelle d'une chambre réactionnelle (102 ou 104) ayant une entrée et une sortie pour une réaction chimique thermique, le procédé comprenant les étapes suivantes :

(a) le passage d'un écoulement de réactif à travers un insert poreux à l'intérieur de ladite chambre réactionnelle (102 ou 104), dans lequel l'écoulement de réactif passe sensiblement complètement à travers ledit insert poreux, dans lequel ledit volume de chambre réactionnelle avec ledit insert poreux a une porosité moyenne inférieure à 1 et une distance de transport de masse inférieure ou égale à 3 mm ;
(b) le transfert de la chaleur de réaction à travers ledit insert poreux, ladite chambre réactionnelle (102 ou 104) ayant une longueur parallèle à l'écoulement de réactif de masse, ladite longueur étant inférieure ou égale à 15 cm, et une hauteur inférieure ou égale à 5 cm ; et
(c) le transfert de chaleur à travers une chambre de transfert de chaleur en contact thermique avec le volume de la chambre réactionnelle, ladite chambre de transfert de chaleur comprenant une entrée et une sortie et un espace ouvert pour l'écoulement d'un fluide d'échange de chaleur, et ladite chaleur étant transférée à travers une paroi entre la chambre de transfert de chaleur et la chambre réactionnelle (102 ou 104).

2. Procédé selon la revendication 1, dans lequel un catalyseur se trouve sur l'insert poreux.

3. Procédé selon la revendication 2, dans lequel ledit insert poreux a une couche interfaciale sur celui-ci, et un métal catalyseur sur la couche interfaciale.

4. Procédé selon la revendication 3, dans lequel ledit insert poreux a une couche tampon entre le support poreux et la couche interfaciale.

5. Procédé selon la revendication 4, dans lequel ladite couche tampon est un oxyde métallique.

6. Procédé selon la revendication 5, dans lequel ledit oxyde métallique est choisi dans le groupe consistant en Al_2O_3, TiO_2 et des combinaisons de ceux-ci.

7. Procédé selon la revendication 6, dans lequel ledit Al_2O_3 est choisi dans le groupe consistant en α-Al_2O_3, γ-Al_2O_3, d'autres phases de Al_2O_3 et des combinaisons de celles-ci.

8. Procédé selon l'une quelconque des revendications 4 à 7, dans lequel ladite couche tampon est déposée en phase vapeur.

9. Procédé selon l'une quelconque des revendications 4 à 8, dans lequel ladite couche tampon comprend une pluralité de sous-couches.

10. Procédé selon l'une quelconque des revendications 3 à 9, dans lequel la couche interfaciale est déposée en solution.

11. Procédé selon la revendication 10, dans lequel lesdits oxydes métalliques déposés en solution sont choisis dans le groupe consistant en γ-Al_2O_3, SiO_2, ZrO_2, TiO_2 et des combinaisons de ceux-ci.

12. Procédé selon l'une quelconque des revendications 3 à 11, dans lequel la couche interfaciale comprend un oxyde métallique.

13. Procédé selon l'une quelconque des revendications 2 à 12, dans lequel ledit matériau catalytique est un métal choisi dans le groupe consistant en les métaux nobles, les métaux de transition et des combinaisons de ceux-ci.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit insert poreux comprend une céramique poreuse.

15. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'insert poreux comprend un monolithe poreux.

16. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel l'insert poreux comprend une mousse métallique.

17. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'insert poreux est en contact thermique avec des parois de la chambre réactionnelle (102 ou 104) et a entre 8 pores par cm et 400 pores par cm.

18. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite réaction chimique thermique est une réaction chimique catalytique.

19. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite réaction chimique thermique est une réaction chimique thermique de reformage à la vapeur et ledit écoulement de réactif comprend un hydrocarbure.

20. Procédé selon la revendication 19, dans lequel ledit insert poreux comprend un support poreux avec un matériau catalytique sur celui-ci, de manière à ce que, pour une conversion à l'équilibre, de 80 % à 100 % dudit hydrocarbure soit converti en un temps de séjour inférieur à environ 50 millisecondes.

21. Procédé selon la revendication 20, dans lequel le temps de séjour est compris entre 11 et 50 millisecondes.

22. Procédé selon la revendication 21, dans lequel l'insert poreux comprend un support de mousse métallique, une couche interfaciale, et dans lequel la réaction a lieu entre 600 et 950 °C.

23. Procédé selon la revendication 22, dans lequel l'hydrocarbure est choisi dans le groupe consistant en le butane, l'essence, l'iso-octane, et le kérosène ; et dans lequel l'hydrogène est produit avec une sélectivité de 89 % à 98 %.

24. Procédé selon l'une quelconque des revendications 1 à 18, dans lequel ladite réaction chimique thermique est une réaction chimique thermique de conversion eau-gaz, et ledit écoulement de réactif comprend de l'eau et du monoxyde de carbone.

25. Procédé selon la revendication 24, dans lequel ledit insert poreux comprend un support poreux avec un matériau catalytique sur celui-ci, et ledit temps de contact est inférieur environ à 100 millisecondes, de manière à ce que la conversion du monoxyde de carbone soit supérieure à environ 50 % de la conversion à l'équilibre.

26. Procédé selon la revendication 25, dans lequel le temps de contact est entre 10 et 100 millisecondes, la conversion est supérieure à 80 %, et le procédé a une sélectivité d'au moins environ 100 % de la sélectivité à l'équilibre vers le dioxyde de carbone.

27. Procédé selon la revendication 26, où l'insert poreux comprend un catalyseur Ru supporté et formé de métal.

28. Réacteur pour obtenir une vitesse de production améliorée par volume d'une chambre réactionnelle (102 ou 104) pour une réaction chimique thermique, le réacteur comprenant :

(a) un insert poreux à l'intérieur de ladite chambre réactionnelle (102 ou 104), dans lequel, lors du fonctionnement, un écoulement de réactif passe sensiblement complètement à travers ledit insert poreux, dans lequel ladite chambre réactionnelle (102 ou 104) avec ledit insert poreux a une porosité moyenne inférieure à 1 et une distance de transport de masse inférieure à 3 mm ; et

(b) ledit volume de chambre réactionnelle ayant une entrée et une sortie, une longueur parallèle à l'écoulement de réactif de masse, ladite longueur étant inférieure ou égale à 15 cm, et une hauteur inférieure ou égale à 5 cm.

29. Réacteur selon la revendication 28, dans lequel un matériau catalytique est sur l'insert poreux.

30. Réacteur selon la revendication 29, dans lequel ledit insert poreux a une couche interfaciale déposée en solution entre le support poreux et le matériau catalytique.

31. Réacteur selon la revendication 30, dans lequel ledit insert poreux a une couche tampon entre le support poreux et la couche interfaciale déposée en solution.

32. Réacteur selon la revendication 31, dans lequel ladite couche tampon est un oxyde métallique.

33. Réacteur selon la revendication 32, dans lequel ledit oxyde métallique est choisi dans le groupe consistant en Al_2O_3, TiO_2 et des combinaisons de ceux-ci.

34. Réacteur selon la revendication 33, dans lequel ledit Al_2O_3 est choisi dans le groupe consistant en α-Al_2O_3, γ-Al_2O_3, d'autres phases de Al_2O_3, et des combinaisons de celles-ci.

35. Réacteur selon l'une quelconque des revendications 31 à 34, dans lequel ladite couche tampon est déposée en phase vapeur.

36. Réacteur selon l'une quelconque des revendications 31 à 35, dans lequel ladite couche tampon comprend une pluralité de sous-couches.

37. Réacteur selon l'une quelconque des revendications 30 à 36, dans lequel la couche interfaciale est déposée en solution.

38. Réacteur selon la revendication 37, dans lequel ledit oxyde métallique déposé en solution est choisi dans le groupe consistant en γ-Al_2O_3, SiO_2, ZrO_2, TiO_2 et des combinaisons de ceux-ci.

39. Réacteur selon l'une quelconque des revendications 30 à 38, dans lequel la couche interfaciale déposée en solution comprend un oxyde métallique.

40. Réacteur selon l'une quelconque des revendications 29 à 39, dans lequel ledit matériau catalytique est un métal choisi dans le groupe consistant en les métaux nobles, les métaux de transition et des combinaisons de ceux-ci.

41. Réacteur selon l'une quelconque des revendications 28 à 40, dans lequel ledit insert poreux comprend une céramique poreuse.

42. Réacteur selon l'une quelconque des revendications 28 à 41, dans lequel l'insert poreux comprend un monolithe poreux.

43. Réacteur selon l'une quelconque des revendications 28 à 40, dans lequel l'insert poreux comprend une mousse métallique.

44. Réacteur selon l'une quelconque des revendications 28 à 43, dans lequel l'insert poreux comprend une mousse métallique ou céramique et est en contact thermique avec des parois de la chambre réactionnelle (102 ou 104) et a entre 8 pores par cm et 400 pores par cm.

45. Récipient (100) pour obtenir une vitesse de production améliorée par volume de chambre réactionnelle d'une chambre réactionnelle (102 ou 104) pour une réaction chimique thermique, le récipient (100) comprenant :

(a) un réacteur selon l'une quelconque des revendications 28 à 44 ; et
(b) une chambre de transfert de chaleur en contact thermique avec le volume de la chambre réactionnelle, ladite chambre de transfert de chaleur ayant une entrée et une sortie, un espace ouvert pour un écoulement de fluide d'échange de chaleur, et une paroi disposée entre la chambre de transfert de chaleur et la chambre réactionnelle (102 ou 104), de manière à ce que, lors du fonctionnement, la chaleur soit transférée à travers ladite paroi.
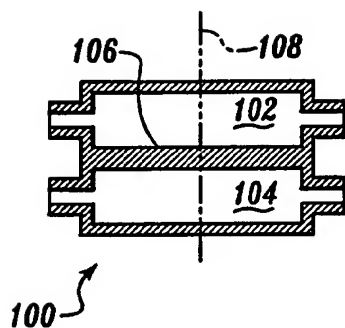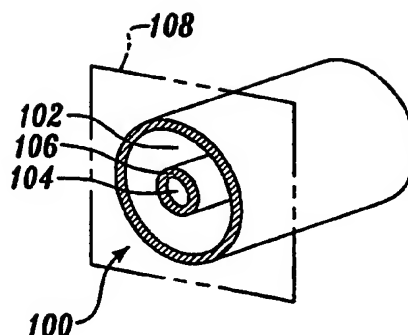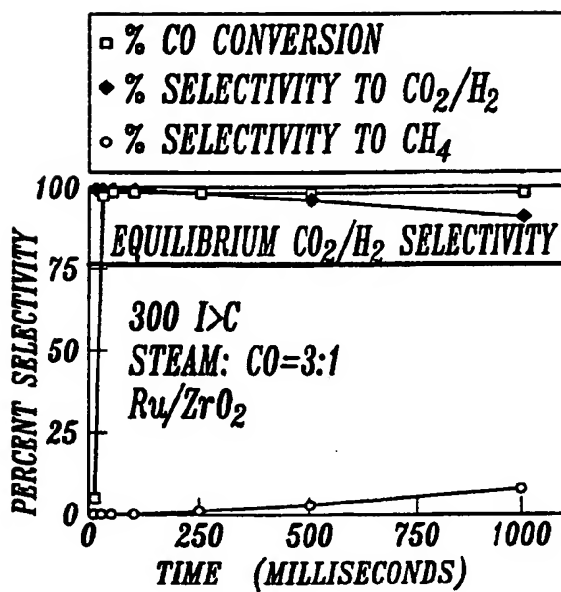
Fig. 1a

Fig. 1b

□ % CO CONVERSION
♦ % SELECTIVITY TO CO_2/H_2
○ % SELECTIVITY TO CH_4

EQUILIBRIUM CO_2/H_2 SELECTIVITY

300 I>C
STEAM: CO=3:1
Ru/ZrO_2

PERCENT SELECTIVITY

TIME (MILLISECONDS)

Fig. 2a

□ % CO CONVERSION
♦ % SELECTIVITY TO CO_2/H_2
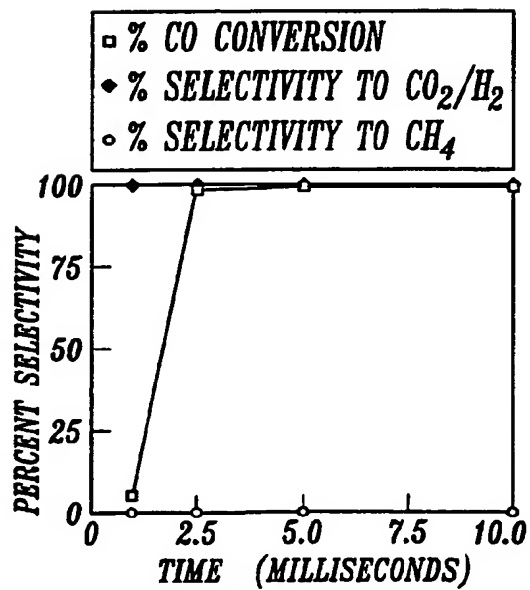○ % SELECTIVITY TO CH_4

PERCENT SELECTIVITY

TIME (MILLISECONDS)

Fig. 2b

CONVERSION AND CO SELECTIVITY VS. TEMPERATURE
FOR %Ru/ZrO₂/Ni AT 10, 50 AND 100 mSEC RESIDENCE
TIME, 3:1 STEAM:CO, 5% CO IN FEED

Fig. 3
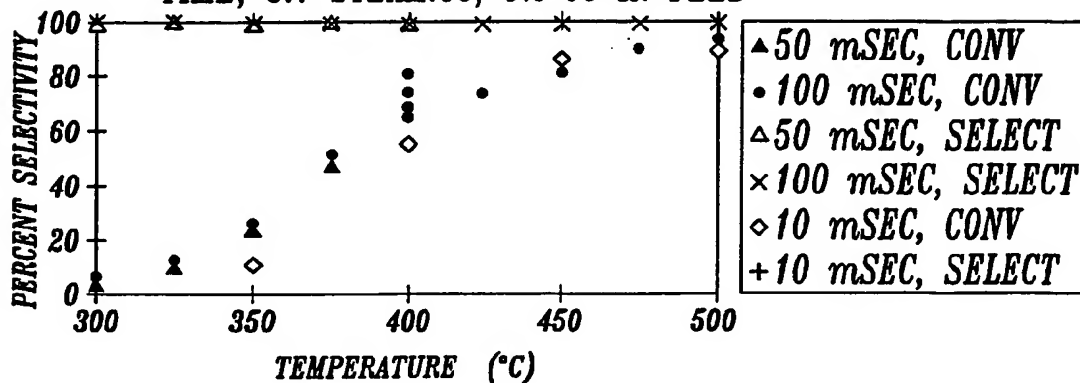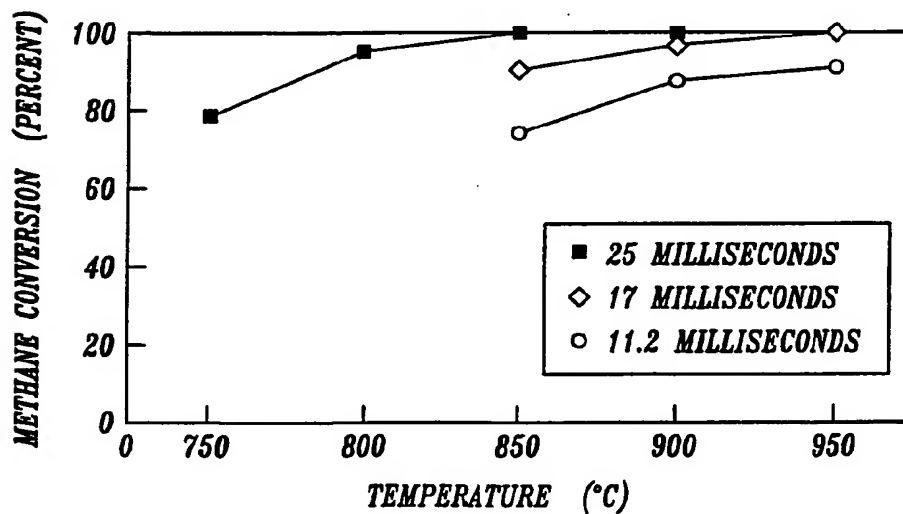

Fig. 4

Fig. 5a

Fig. 5b